

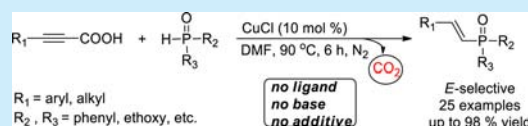
Copper-Catalyzed Decarboxylative C–P Cross-Coupling of Alkynyl Acids with *H*-Phosphine Oxides: A Facile and Selective Synthesis of (*E*)-1-Alkenylphosphine Oxides

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S Supporting Information

ABSTRACT: A novel and efficient copper-catalyzed decarboxylative cross-coupling of alkynyl acids for the stereoselective synthesis of *E*-alkenylphosphine oxides has been developed. In the presence of 10 mol % of CuCl without added ligand, base, and additive, various alkynyl acids reacted with *H*-phosphine oxides to afford *E*-alkenylphosphine oxides with operational simplicity, broad substrate scope, and the stereoselectivity for *E*-isomers.

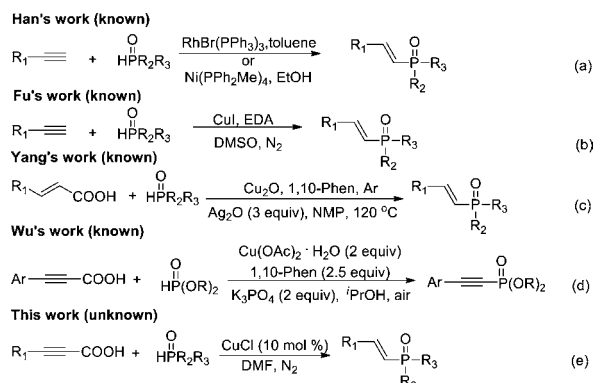


The utility of alkenylphosphine oxides has increased enormously over the past several years for their important roles. For example, they can be used as biologically active compounds,¹ and the main building blocks of phosphorus-containing materials,² and the key precursors for the preparation of valuable phosphine ligands.³ Moreover, they could also provide a variety of synthetically elaborated bifunctional adducts by the addition of heteroatom nucleophiles,⁴ carbanion species,⁵ and carbon-centered radicals⁶ to the olefinic bonds. Recently, a few transition-metal-catalyzed methods for the synthesis of alkenylphosphine oxides involving the use of palladium,⁷ copper,⁸ nickel,⁹ rhodium,¹⁰ and ytterbium-imine complex¹¹ based catalytic systems have continuously emerged. Among them, transition-metal-catalyzed addition of P(O)H compounds to alkynes has emerged as the most commonly used and powerful approach for making alkenylphosphine oxides. In 2001 and 2004, Han reported the Rh- and Ni-catalyzed additions of P(O)H compounds to alkynes (Scheme 1a).^{10a,9a} In 2007, Fu and co-workers developed a CuI/EDA catalytic system for the synthesis

of alkenylphosphine oxides (Scheme 1b).^{8b} Despite their usefulness, almost all of these methods need well-defined ligands and excess bases or additives, and these protocols have common problems such as relatively strict reaction conditions, excess reagents, poor substrate scope, or lack of stereoselectivity, thus increasing the cost and limiting the applications of these methods.

In recent years, transition-metal-catalyzed decarboxylative coupling reactions as a new synthetic strategy have attracted increasing attention in the formation of C–C and C–heteroatom bonds.¹² In particular, various valuable P-alkenylated and P-alkynylated motifs can be readily obtained through decarboxylative C–P cross-coupling.^{8d,13} In 2011, Yang's group first reported the synthesis of alkenylphosphine oxides via a Cu-catalyzed decarboxylative coupling of alkenyl acid (Scheme 1c).^{8d} It is noteworthy that as a practical alternative, using arylpropionic acids instead of terminal alkynes is safer and more attractive because arylpropionic acids are usually solids without an unpleasant smell and are convenient to synthesize, store, and transport.¹⁴ On the basis of this viewpoint, very recently, Wu's group¹³ and Yang's group^{8d} fulfilled the decarboxylative coupling of arylpropionic acids with P(O)H to construct a Csp–P bond with the assistance of a Cu or Cu/Pd cocatalyst system, respectively (Scheme 1d). Notably, these reactions only afforded alkenylphosphorus products and did not produce alkenylphosphorus compounds. To the best of our knowledge, the example of alkenylphosphine oxide formation via decarboxylative coupling of alkynyl acids has yet to be reported (Scheme 1e). On the other hand, a ligand-free, base-free, and additive-free catalysis system would be more attractive both from economic and industrial points of view as compared to the ones-containing system. As part of our ongoing efforts to develop environmentally friendly new methodologies for the P–C bond formation,^{9b,15} we herein report the first example of a single-

Scheme 1. Transition-Metal-Catalyzed C–P Bond-Forming Reaction



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step preparation of stereoselective (*E*)-alkenylphosphine oxides by a simple copper-catalyzed decarboxylative coupling of various alkynyl acids with P(O)H compounds under ligand-free, base-free, and additive-free conditions.

Phenylpropionic acid (**1a**) and H(O)PPh₂ (**2a**) were chosen as the model substrates to screen and optimize the catalysis conditions as shown in Table 1. Initially, the reaction of **1a** (1.5

Table 1. Optimization of the Reaction Conditions^a

$\text{Ph}-\text{C}\equiv\text{C}-\text{COOH} + \text{H}-\text{P}(\text{O})(\text{Ph})_2 \xrightarrow[\text{solvent, 6 h}]{\text{catalyst, ligand, base}} \text{Ph}-\text{CH}=\text{CH}-\text{P}(\text{O})(\text{Ph})_2$					
entry	catalyst	ligand	base	solvent	yield (<i>E</i> , %) ^b
1	CuI	L-proline	Cs ₂ CO ₃	DMSO	84
2	CuI	L-proline	<i>t</i> -BuOK	DMSO	66
3	CuI	L-proline	Et ₃ N	DMSO	91
4	CuI	L-proline	DMAP ^c	DMSO	90
5	CuI	L-proline		DMSO	92
6	CuI			DMSO	96
7	CuI			toluene	0
8	CuI			dioxane	trace
9	CuI			DMF	98
10	CuCl			DMF	97
11	Cu(OAc) ₂			DMF	95
12	CuCl			DMF	45 ^d
13	CuCl			DMF	trace ^e
14	CuCl			DMF	97 ^f
15	CuCl			DMF	94 ^g
16	CuCl			DMF	55 ^h
17	CuCl			DMF	92 ⁱ
18	CuCl			DMF	76 ^j

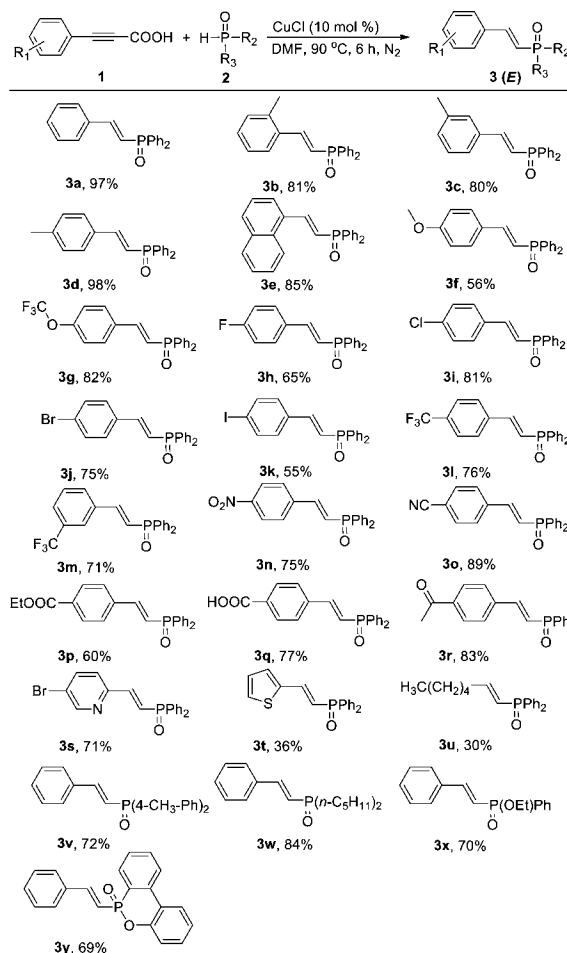
^aReaction conditions: phenylpropionic acid **1a** (0.75 mmol), H(O)-PPh₂ **2a** (0.5 mmol), catalyst (10 mol %), ligand (15 mol %), solvent (2 mL), base (1.2 equiv) at 90 °C for 6 h under N₂. ^bIsolated yield based on **2a**. Only *E*-isomer **3a** was detected by in situ ³¹P NMR and ¹H NMR analysis of crude reaction mixtures. ^cDMAP = (4-*N,N*-dimethylpyridine). ^dAt 60 °C. ^eAt rt. ^fUsing 1.2 equiv of **1a** (0.6 mmol). ^gUsing 1.0 equiv of **1a** (0.5 mmol). ^hUsing 2 mol % of CuCl. ⁱUsing 6 mol % of CuCl. ^jUnder air.

equiv) with **2a** (1 equiv) was performed in DMSO (2 mL) at 90 °C for 6 h under nitrogen in the presence of CuI (10 mol %), L-proline (15 mol %), and Cs₂CO₃ (1.2 equiv). Gratifyingly, the desired product (*E*)-styryl diphenylphosphine oxide (**3a**) was obtained in a high yield of 84% (Table 1, entry 1). Encouraged by this promising result, various bases were further investigated. It was found that a strong base like *t*-BuOK afforded **3a** in a lower yield of 66% (Table 1, entry 2), but when some weak bases such as Et₃N and DMAP were used, the yield could increase to 91% and 90% yields, respectively (Table 1, entries 3 and 4). In order to test the role of the base, the reaction was carried out under base-free conditions (Table 1, entry 5). To our delight, the transformation could still proceed smoothly to provide **3a** in an excellent yield of 92%, clearly indicating that the base was not essential to this coupling. Subsequently, we checked the effect of the ligand, and without the ligand, the yield of **3a** could be up to 96%, demonstrating that the addition of the ligand is less effective (Table 1, entry 6). A screening of the solvents such as toluene, 1,4-dioxane, and DMF illustrated that DMF was the best choice for this reaction and enhanced the yield up to 98% (Table 1, entries 7–9). To advance the process further, other copper salts including CuCl and Cu(OAc)₂ were detected, with the finding

that they could also promote the reaction efficiently to give 97% and 95% yields, respectively (Table 1, entries 10 and 11). Thus, we chose CuCl as the best catalyst owing to the lower price and similar yield in contrast to CuI (Table 1, entry 10). Decreasing the reaction temperature to 60 °C and rt would lead to poor yields (Table 1, entries 12 and 13). Noting that decreasing the load of **1a** to 1.2 equiv was sufficient to produce an excellent yield of 97% (Table 1, entry 14). However, using 1 equiv of **1a** resulted in a slight decrease of the yield (Table 1, entry 15). The CuCl loading was also evaluated, and using 2 and 6 mol % of CuCl gave **3a** in 55% and 92% yields, respectively (Table 1, entries 16 and 17). Under an open air atmosphere, the yield decreased to 76% due to the oxidation of **2a** to Ph₂P(O)OH (Table 1, entry 18). Notably, this novel decarboxylative coupling only produced the *E*-isomer determined by in situ ³¹P NMR and ¹H NMR analysis, without the observation of other regio- or stereoisomers. Moreover, the ligand, the base, and the additive are not needed, and milder reaction conditions are possible.

Under the optimized conditions shown in footnote *a*, Scheme 2, the substrate scope of this coupling was surveyed. As shown in Scheme 2, various arylpropionic acids bearing different electron-withdrawing and electron-donating substituents were all

Scheme 2. Decarboxylative Cross-Coupling of Alkyne Acids with P(O)H^{a,b}



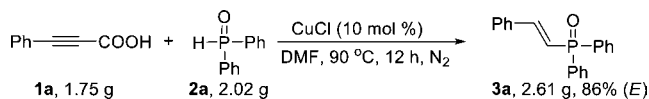
^aReaction conditions: alkynyl acid **1** (0.6 mmol), P(O)H **2** (0.5 mmol), CuCl (10 mol %), and DMF (2.0 mL) at 90 °C for 6 h under nitrogen. ^bIsolated yield. Only *E*-isomer **3** was determined by in situ ³¹P NMR and ¹H NMR analysis of crude reaction mixtures.

efficiently reacted with diphosphine oxide **2a** via decarboxylative cross-coupling reactions to afford anti-Markovnikov coupling products (*E*)-1-alkenylphosphine oxides in moderate to good yields of 55–98% with the stereoselectivity for *E*-isomers based on the analysis of in situ ^{31}P NMR and ^1H NMR spectra (Scheme 2, **3a–r**), revealing that this novel Cu-catalyzed decarboxylative C–P cross-coupling is a general and powerful tool for the synthesis of various valuable P-alkenylated motifs. Importantly, a variety of functional groups, such as methyl, aryl, alkoxy, fluoro, chloro, bromo, iodo, trifluoromethyl, nitro, cyano, carbonyl, and carboxyl groups, were all well tolerated, indicating that electronic effects and steric hindrance are not evident in this transformation. Notably, the propiolic acid moiety represented a higher chemoselectivity over the chlorine, bromine, and reactive iodine atoms as leaving groups under the standard reaction conditions, producing the desired products (**3i–k**) in 55–81% yields. Thus, the chemoselectivity may be further applied for the preparation of more complex molecules through stepwise coupling of arylpropionic acids and halides. Interestingly, a carboxylic acid substrate having a carboxyl unit without needing any protection could also be used in the reaction to give the desired product **3q** in a good yield of 77%. The heterocyclic propiolic acid having a pyridine ring could also be compatible for this reaction, affording the desired product **3s** in 71% yield. However, the sulfur-containing heterocyclic propiolic acid could only provide the product **3t** in 36% yield, which may be attributed to the sulfur species dramatically deactivating the catalyst. In addition, the present protocol is less effective for aliphatic alkynyl acid; for example, 2-octynoic acid **2u** only gave **3u** in 30% yield.

To further extend the scope of this reaction, the alkenylation of various P(O)H substrates was also investigated (Scheme 2, **3v–y**). In regard to the H-phosphine oxides, apart from **2a**, di-*p*-tolylphosphine oxide (**2b**) and aliphatic dipentylphosphine oxide (**2c**) were all suitable substrates, and the corresponding products **3v** and **3w** were obtained in 72% and 84% yields, respectively. In addition, ethyl phenylphosphinate (**2d**) and 6*H*-dibenzo[*c,e*]-[1,2]oxaphosphinine 6-oxide (**2e**) were also detected and produced the desired products **3x** and **3y** in good yields. However, H-phosphonates such as diethyl phosphonate only provided a trace amount of the desired product in the present catalytic system.

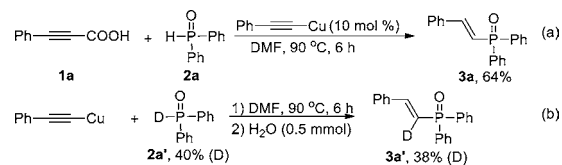
It is noteworthy that this Cu-catalyzed decarboxylative coupling of alkynyl acids could also be effectively scaled up with the high efficiency. For example, in the presence of CuCl (10 mol %), **1a** (12 mmol) reacted with **2a** (10 mmol) in DMF at 90 °C for 12 h to afford the corresponding product **3a** in 86% yield (Scheme 3).

Scheme 3. Gram-Scale Synthesis of **3a**



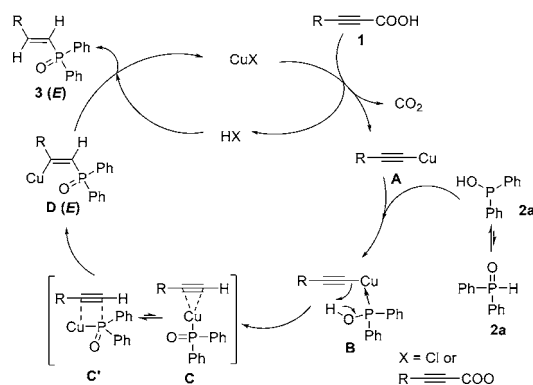
To understand the mechanism more clearly, some control experiments were carried out (Scheme 4). When 10 mol % of (phenylethynyl)copper instead of CuCl was employed as the catalyst, a 64% yield of **3a** was isolated, which demonstrated that (phenylethynyl)copper might be a key intermediate in this reaction and was essential for the transformation (Scheme 4a). Indeed, the (phenylethynyl)copper as a yellow precipitate was observed during the reaction process. In addition, a deuterium

Scheme 4. Mechanism Study Experiments



labeling study was also performed as shown in Scheme 4b. It was found that when the substrate **2a'** (40% D) was treated with 1.2 equiv of (phenylethynyl)copper, almost all deuterium incorporation into **3a** was observed (**3a'**, 38% D), clearly illustrating that the hydrogen atom of the α -position of the product **3** came from P(O)–H. On the basis of these experimental results and previous reports,¹⁶ a plausible mechanism for this coupling reaction is proposed (Scheme 5). First, the decarboxylative reaction of **1**

Scheme 5. Plausible Reaction Mechanism



took place with the assistance of CuCl to form alkynyl copper intermediate **A** and released one molecular CO_2 and HCl . Then, the coordination of **2** (in the form of the trivalent phosphine oxide **2'**) to **A**, affording **B**, was reasonable.^{15a} Subsequently, a proton transfer from oxygen atom to Csp atom led to generation of a three-membered-ring transition state **C**. Next, **C** underwent a four-centered transition state **C'**^{16f} to give a thermodynamically more stable alkenyl copper intermediate **D** with the *E* configuration due to the steric hindrance and the cis-addition of $(\text{Ph})_2\text{P}(\text{O})\text{Cu}$ to phenyl acetylene, which are the main reasons for the selection of an all-*trans* configuration for the product **3**. Finally, the protonolysis of intermediate **D** with **1** or HCl resulted in the generation of the desired product **3** and catalytically active Cu(I) species to fulfill the catalytic cycle.

In conclusion, we have successfully developed the first facile and efficient method for the preparation of (*E*)-1-alkenylphosphine oxides and (*E*)-1-alkenylphosphinate esters through copper-catalyzed decarboxylative C–P cross-coupling of various alkynyl acids with H-phosphine oxides and H-phosphinate esters. Importantly, this novel method not only expands our understanding of the decarboxylation but also affords a powerful synthetic tool for simple synthesis of valuable (*E*)-P-alkenylated motifs. Moreover, only in the presence of CuCl without needing a base, a ligand, and an additive, the transformation could proceed smoothly. In addition, the use of inexpensive CuCl catalyst, using readily available and stable alkynyl acids only producing CO_2 , the remarkable functional group tolerance and high stereoselectivity for *E*-isomers mean that this facile protocol will be attractive for academia and industry. Further mechanistic investigations and synthetic applications are currently underway.

■ ASSOCIATED CONTENT

■ Supporting Information

General experimental procedure and characterization data of the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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